ELECTRICAL AND OPTICAL PROPERTIES OF COLLOIDAL QUANTUM DOTS AND QUANTUM DOT NETWORKS: ROLE OF SURFACE STATES AND USING BIOMOLECULAR LINKS IN NETWORK ASSEMBLY

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ABSTRACT

The objectives of this paper are to determine the role of surface states in determining the electrical and optical properties of semiconductor quantum dots in colloidal suspensions, and to use biomolecules to facilitate the chemically-directed assembly of quantum dots networks with densities approximating 10^{17} cm^{-3}. Absorption spectra and photoluminescence (PL) spectra of colloidal cadmium sulfide (CdS) quantum dots are analyzed to investigate the role of surface states in determining the electrical and optical properties of these semiconductor quantum dots. In addition, this work demonstrates the utility of using glycine-glycine-glycine-cysteine (GGGC) peptides and crossing-linking chemical reactions to achieve integrated networks of ZnS-coated CdSe quantum dots and CdS quantum dots.

I. INTRODUCTION

Suspensions of colloidal semiconductor quantum dots have a variety of potential applications spanning fields as diverse as nanoelectronics, bioengineering, and optoelectronics. In order to realize such potential applications it is essential that the electrical and optical properties of such quantum dot be understood in a variety of environments including electrolytic environments. Moreover, the chemically-directed assembly of such nanoscale quantum dots portends the fabrication of integrated semiconductor systems containing approximately 10^{17} quantum dots per cm^{-3}. This paper provides experimental and theoretical results bearing of the electrical and optical properties of such quantum dot suspensions and reports on the chemically-directed assembly of an ensemble of quantum dots.

II. RESULTS

Concerning the electrical and optical properties of semiconductor quantum dots in colloidal suspensions, results include: (a) the finding that the wavelength for the onset of the optical absorption of such a colloidal suspension shifts as the concentration of the electrolyte is changed; and (b) binding of selected amino-acid based biomolecules to the surface states of these quantum dots leads to quenching of the photoluminescence (PL) from these quantum dots. As depicted in Figures 1a and 1b, bandbending associated with the field caused by an internal polarization of these quantum dots leads to a shift in the absorption threshold as a function of the electrolytic concentration. As specific examples of the polarizations possible, the spontaneous polarizations of selected würtzite structures are summarized in Table I.

Table 1. Bandgaps and spontaneous polarizations of selected würtzite structures.

Compound Semiconductor	Bandgap, (eV) (direct bandgaps unless otherwise specified)	Spontaneous Polarization, (C/m^2)
AlN		- 0.081
CdS hexagonal	2.4 E_g (A) 2.5 E_g (B) 2.55 E_g (C)	0.002
CdS cubic	2.5	
CdSe hexagonal	1.75 E_g (A) 1.771 E_g (B) 2.17 E_g (C)	0.006
CdSe cubic	1.9	
GaN	3.36	- 0.029
ZnO	3.35	- 0.07

To estimate the bandbending, $dE_c(x)/dx$, in a nanocrystal caused by an internal polarization, it is possible to use the well-known formula, $dE_c(x)/dx = qE$. As an example, for a one-dimensional CdS square well, the lowest eigenenergy is approximated by [1],

$$E_{square} = E_{gap} + \frac{\left(\frac{h}{d}\right)^2}{8m_e} + \frac{\left(\frac{h}{d}\right)^2}{8m_h} - \frac{3.536e^2}{4\pi\varepsilon\varepsilon_0 d} \quad (1)$$

where d is the width of the quantum well, h is Planck's constant, the effective mass of the electron, m_e, is taken to be 0.235 of the free electron mass (9.11×10^{-31} kg), the effective mass of the hole, m_h, is taken to be 1.35 of the free hole mass, ε is the relative dielectric constant of CdS

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--- 5.7, ε_o is the permittivity of free space --- 8.85×10^{-12} F/m, and e is the electron charge --- 1.6×10^{-19} C. The first term in this expression represents the bandgap of bulk CdS, and the second and third terms represent the confinement energies, respectively. The fourth term represents the Coulomb binding energy of the exciton in CdS (Lippens and Lannoo, 1989).This expression holds when there is no bandbending due to the polarization field in CdS. Specifically, this expression holds when flat band conditions prevail as would be the case if the surrounding electrolyte were to completely screen the field associated with the polarization. This screening may be thought of in terms of the anion and cation induced screening of the effective surface charge given by $|P_s|\cos\theta$, where P_s is the internal polarization of the quantum dot and θ ranges from 0 to π and is the angle measured from the c-axis. The nanocrystal behaves as a dipole with positive charge concentrated near one pole, and negative charge concentrated near the other pole. The equatorial plane is electrically neutral. The anions and cations in the electrolyte will attempt to screen the polarization-induced dipole. In the case where the electrolyte has a density so low that it does not screen the polarization, the ground state energy is given approximately by that of a triangular quantum well: (Davydov, 1966)

$$
E_{triangle} = E_{gap} + \left(\frac{h^2}{8\pi^2 m_e}\right)^{\frac{1}{3}} \left(\frac{9\pi F}{8}\right)^{\frac{2}{3}}
$$

$$
+ \left(\frac{h^2}{8\pi^2 m_h}\right)^{\frac{1}{3}} \left(\frac{9\pi F}{8}\right)^{\frac{2}{3}} - Fd - \frac{3.536 e^2}{4\pi\varepsilon\varepsilon_0 d}
$$

(2)

where F is the electric field associated with the quantum-dot polarization. The corresponding wavelengths, λ_{square} and $\lambda_{triangle}$ are given by, $\lambda_{square} = hc/E_{square}$ and $\lambda_{triangle} = hc/E_{triangle}$. Evaluation of these expressions for CdS results in shift in the absorption edge, and therefore the photoluminescence spectrum, of a few percent. The shift in the optical absorption edge as a function of electrolytic concentration is yet another effect resulting from the interaction between the nanocrystals and the electrolytic environment. More specifically, Figure 1a depicts bandbending due to polarization in the presence screening of anions and cations resulting from the 5 mM concentration of NaCl present in the electrolytic suspension of semiconductor quantum dots. In addition, Figure 1b, illustrates bandbending due to polarization when there is no electrolytic screening. Figure 2 illustrates the shift in the threshold for absorption as a function of the electrolytic concentration. In another surface-state related effect, Figure 3 depicts the observed quenching of the photoluminecence intensity of a suspension of colloidal cadmium sulfide (CdS) quantum dots as the CGGGIKVAV (denoted by IKVAV) peptide concentration is increased from 0 to 2 mg in a 5 mL volume of a 5 mM CdS suspension. A possible mechanism for this quenching effect may be presence of surface absorbed peptides that results in greater surface localization of charges. In any case, the relative change in the PL intensity as a function of surfactant concentration portends applications in the determination of the concentrations of peptides present in the colloidal suspension.
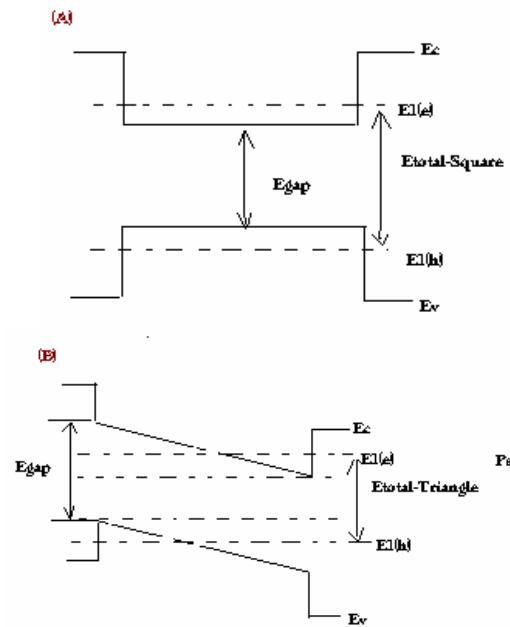

Figure 1. (A) Bandbending due to internal polarization in the presence of electrolytic screening. (B) Bandbending due to the polarization field in the absence of electrolytic screening.

These and related surface-state effects are of importance in determining a number of electrical and optical properties underlie a number of applications of these nanocrystals in sensing electrolytic concentrations, in tuning optical transition energies, and in the potential control of quantum dot blinking. The colloidal CdS nanocrystals used in this study were synthesized using techniques of colloidal chemisty (Chen et al., 2000; Alexson et al., 2004). Specifically, a 5mM solution of $CdCl_2$ (36.6 mg of $CdCl_2$ in 40 mL of H_2O) was titrated with mercaptoacetic acid until a pH of 2 was achieved. Concentrated NaOH was then added dropwise until a pH of 7 resulted. On mixing this solution with a 5 mM solution of $Na_2S \cdot 9H_2O$, a yellow colloidal suspension of CdS was formed. As shown in Figure 4, the CdS quantum dots exhibit broadband emission from about 550
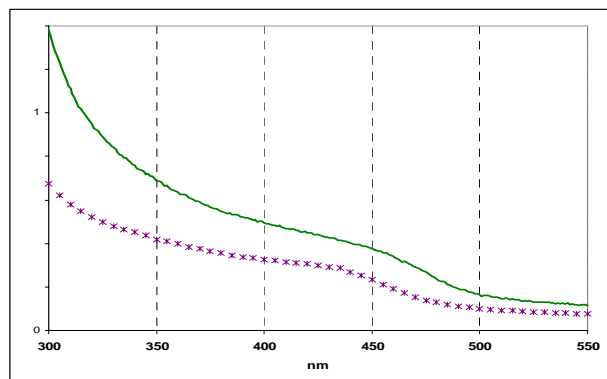
Figure 2. Shift in the absorption threshold for a suspension of colloidal CdS quantum dots for (a) a 5 mM concentration of NaCl (lower curve) and (b) for the same suspension diluted by an order of magnitude.
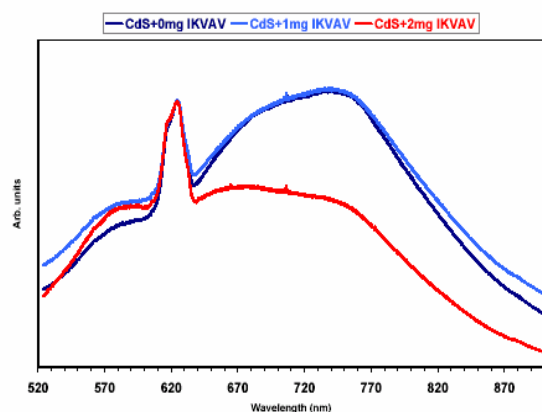

Figure 3. Quenching of PL intensity with increasing concentrations of IKVAV-based peptides.

nm to 900 nm due to surface state emission as revealed by photoluminescense (PL) spectra taken using a 514 nm Ar+ laser source to ensure the sub-bandgap excitation of the CdS-peptide complexes; the CdS surface states emit well above the relatively weak CdS band-to-band transition that occurs at about 440 nm (Alexson et al., 2004).

Concerning the chemically-directed assembly of ensembles of quantum dots using biomolecular links, this work demonstrates that ZnS-coated CdSe quantum dots and CdS quantum dots may be assembled layer-by-layer on a Au substrate --- in this case a 96-micrometer-diameter Au wire --- using glycine-glycine-glycine-cysteine (GGGC) peptides as biomolecular links. The steps used to fabricate these ensembles are summarized in the following discussion. COOH-functionalized ZnS-coated CdSe quantum dots were obtained from Evident Technologies, Inc.; the emission from these surface-passivated dots is almost entirely due the band-to-band line at 525 nm. The functionalization of the colloidal
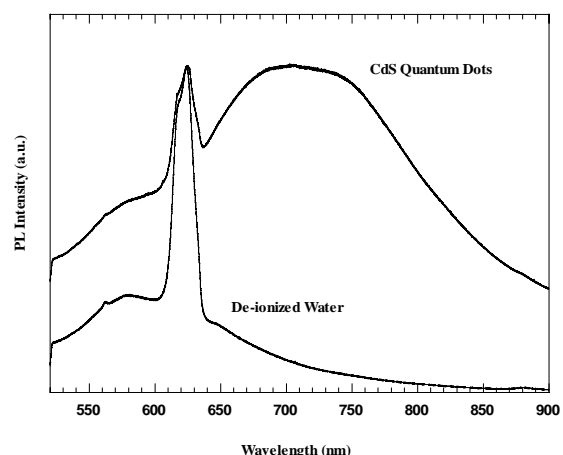

Figure 4. Photoluminescence spectrum of CdS quantum dots.

CdSe-ZnS quantum dots with peptides was accomplished through simple covalent bonding by using a common cross-linking reagent – EDC(1-ethy-3-(3-dimethylamino propyl) carbodiimide) to bind the amine terminus of the glycine (G) end group to the carboxyl groups on the COOH-functionalized ZnS-coated CdSe quantum dots by introducing 0.5 mg/mL of GGGC as well as the EDC agents into the 0.5 mM/mL ZnS-coated CdSe suspension. These peptides were prepared at the Protein Research Laboratory of the University of Illinois at Chicago by widely-used FMOC (9-fluorenylmethyloxycarbonyl) solid phase synthesis techniques (Gields and Noble, 1990; Chan and White, 2000) and were characterized by mass spectrometry. The layered CdSe-ZnS/CdS/CdSe-ZnS/CdS were prepared by dipping an Au wire alternatively in the CdSe-ZnS-GGGC suspension and in the CdS suspension. In the case where the functionalized wire is dipped in the CdS suspension, the cysteine (C) end group binds to the CdS quantum dots through a thiol bond. As a result of this thiol bond between the CdS quantum dot and the cysteine amino acid, the binding of peptides to quantum dots is very effective.

To verify the formation of successive layers of CdSe-ZnS and CdS, fluorescence microscopy was used to image the Au wire with its surface coatings of CdSe-ZnS quantum dots and CdS. Typical fluorescence microscope images, taken with a Nikon E600 fluorescence microscope with a 20X objective are shown in Figures 5 and 6. The incident light was filtered with a Chroma filter that passed radiation in a 350-450 nm window. For the fluorescence image of Figures 5 and 6, light was collected at 525 nm ± 20 nm and 585 nm ± 40 nm, respectively.

The schematic of a CdSe-ZnS/CdS/CdSe-ZnS/CdS-coated Au wire corresponding to the structures imaged in Figures 5 and 6 is shown in Figure 7. The cysteine end groups on the CdSe/ZnS-GGGC structures facilitates the
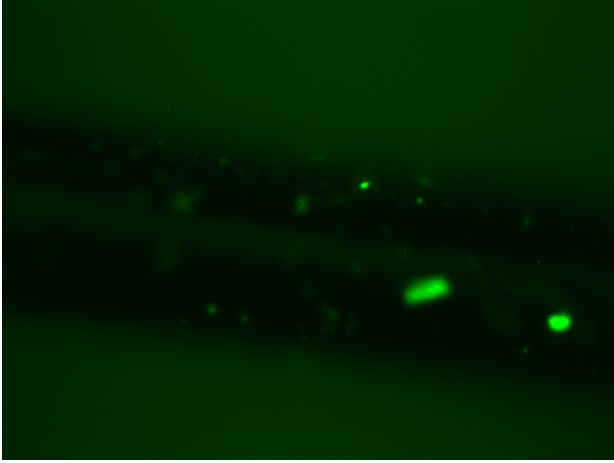
Figure 5. Fluorescence image of CdSe-ZnS/CdS/CdSe-ZnS/CdS-coated Au wire with a collection window of 525 ± 20 nm.

Figure 6. Fluorescence image of CdSe-ZnS/CdS/CdSe-ZnS/CdS-coated Au wire with a collection window of 585 ± 40 nm.
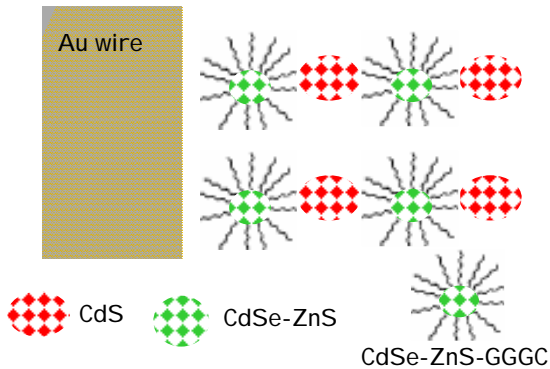

Figure 7. Schematic of CdSe-ZnS/CdS/CdSe-ZnS/CdS-coated Au wire.

binding of the first layer of quantum dots to the Au wire through the binding affinity of the sulfur in the thiol group. The subsequent binding of the CdS quantum dots occurs as a result of their affinity for binding with the cysteine on the CdSe/ZnS-GGGC structures through the thiol bond. The second, third, and successive layers are then bound to the quantum dot network based on the same chemical binding sequences. The scheme illustrated in Figure 7 is one of many possible schemes for the chemically-directed assembly of quantum-dot ensembles.

III. CONCLUSIONS

This paper has outlined the use of chemically-directed assembly to integrate nanoscale quantum dots at densities approximating 10^{17} cm^{-3}. The potential applications of such structures are numerous and they include: structures for terascale electronic integration with biomolecular links, THz nanomechanical structures, and THz sensors (Stroscio and Dutta, 2001; Alexson et al., 2004; Storscio et al., 2004). Indeed, these techniques open ways to fabricate prototypes of a quantum-dot-based electronic system exhibiting integration on the terascale based upon layer-by-layer biomolecule-based chemically-directed assembly of ensembles of semiconductor quantum dots. In a specific embodiment of such a system, peptides with suitable end groups have been used to assemble layers of quantum dots that alternate between ZnS-coated CdSe and uncoated CdS. The ensembles of nanoscale quantum dots fabricated with biomolecular links contain approximately 10^{17} quantum dots per cm^3. Moreover, it has been shown using optical absorption spectra of related colloidal systems indicate that: (a) binding of selected amino-acid based biomolecules to the surface states of these quantum dots leads to quenching of the photoluminescence (PL) from these quantum dots, and (b) the wavelength for the onset of the optical absorption of such a colloidal suspension shifts as the concentration of the electrolyte is changed.

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